Quantum Chemical Calculations of 3-Methoxybenzonitrile for NLO Applications

N.Y.Sugirtha Suni, R.Ganapathi Raman

Abstract: ***The optimized molecular geometry, lowest unoccupied molecular orbital energy (LUMO) Mulliken atomic charges, polarizability, highest occupied molecular orbital energy(HOMO),first hyper polarizability of 3-methoxybenzonitrile were predicted with the aid of density functional theory (DFT) calculations with B3LYP using 6-311++G(d,p), cc-pvdz and Aug-cc-pvdz basis set. Calculated HOMO-LUMO energy gap and first hyper polarizability confirm a nonlinear optical property of a material. DFT was studied the Natural bond orbital analysis, electrostatic potential and several thermo dynamical parameters.***

Index Terms**: *3-methoxybenzonitrile, Density Functional Theory(DFT), HOMOLUMO, electrostatic potential.***

I. INTRODUCTION

Benzonitrile is an aromatic organic compound. Benzonitrilederivatives find application in industries and medical field [1, 24]. Benzonitrile compounds are used as preservatives for a food product. In industry, they are used for preparing the dye named aniline blue. In a medical field, many benzonitrile derivatives in solid form are used as a urinary antiseptic and vapor form are used for protecting bronchial tubes [2]. Since benzonitrile derivatives have wide applications, many studies have been presented on such compounds.

A.Prakasam have reported the molecular structure of 4-methoxybenzonitrile [3]. Murugan reported the vibrational frequencies and molecular structure of 2-fluoro-6- methoxybenzonitrile [4]. N.Sundaraganesan et. al investigated a structural and vibrational modes of 2-fluoro-5- methylbenzonitrile [5]. First hyperpolarizability and the HOMO-LUMO energy are the most important tools that confirm the NLO activity of a compound.

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II. MATERIALS AND METHODS

Entire calculations were performed using Gaussian 09 program package with the aid of DFT with B3LYP using 6-311++G(d,p), cc-pvdz and Aug-cc-pvdz basis set and the results were viewed using GAUSS VIEW program [6]. Time-dependent DFT found HOMO - LUMO energy. NBO analysis was done to explain the interactions between filled and vacant orbitals. The electrostatic potential plot was drawn by MOLKEL. Also, polarizability, hyperpolarizability, and some thermodynamic properties were studied using the same basis sets.

III. RESULTS AND DISCUSSION

A. Geometric Structure

The optimized geometric structure of 3-methoxy benzonitrile is illustrated in Fig.1. The optimized parameters are calculated using B3LYP 6-311++G(d,p), cc-pvdz and Aug-cc-pvdz basis sets. The calculated geometrical parameters like bond length, bond angle and dihedral angle are listed in Table 1. These parameters are utilized to elucidate other properties of the material under study.

B. NBO analysis

NBO analysis is an important tool for knowing the intra and intermolecular bonding and the interaction between bonds and it acts as a basic factor for studying the transfer of charge in the molecular system [7]. NBO study was done on the title molecule by B3LTYP/6-311++G(d,p) level to confirm an intramolecular interaction in a molecule. The electron donors and acceptors interaction are more intensive for larger values of E (2). The system is stable because of the transfer of intramolecular charges that happens by the intramolecular interaction which is caused by the overlap of orbitals between bonding π(C5 - C6),π (C7 - C8) and antibonding π*(C7 - C8),π*(C3 - C4) orbitals. The NBO analysis of 3-methoxybenzonitrile is presented in Table (2).

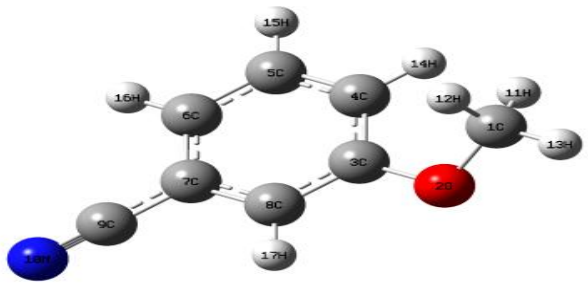

FIG.1.OPTIMIZED GEOMETRICAL STRUCTURE OF 3-METHOXYBENZONITRILE

C. Mulliken atomic charges

Mulliken atomic charge analysis plays a vital part in applying the quantum chemical studies on molecular systems since atomic charge changes the dipole moment, molecular polarizability and electronic structure of molecular system [8]. Mulliken charges calculated using B3LYP 6-311++G(d,p), cc-pvdsz and Aug-cc-pvdz are listed in Table 3. Mulliken atomic charges graph is illustrated in Fig.2. Table 3 reveals that there is change in charge with basis set, which is due to polarization [9]. All the hydrogen atoms exhibit positive charge, the nitrogen , oxygen atom exhibit negative charge in the basis set B3LYP 6-311++G(d,p). This suggests the occurrence of intermolecular interaction in the molecule in solid forms [10]. From the charge calculation it is clear that the nitrogen atom is having negative charge acts as the donor atom and the ring hydrogen atom having positive charge acts as the acceptor atom.

D. Polarizability and Hyperpolarizability

The behavior of a system under an enforced electric field can be studied by itsPolarizability and hyperpolarizability. The NLO property of a compound can be studied using these parameters. The first hyperpolarizability calculated for the compound under study is 2.291x10-30esu which is 7.65 times than urea (0.2991x10-30esu) a standard nonlinear material [11]. Calculated dipole moment, polarizability and hyperpolarizability are given in Table 4.

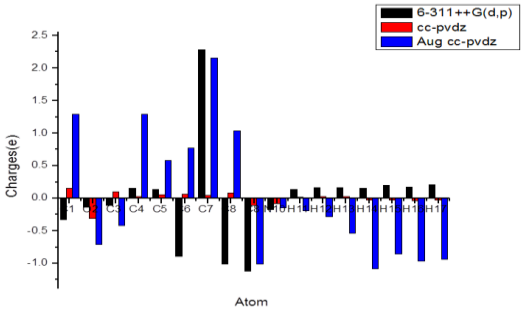

FIG.2.A PLOT OF MULLIKEN ATOMIC CHARGES OF 3-METHOXYBENZONITRILE

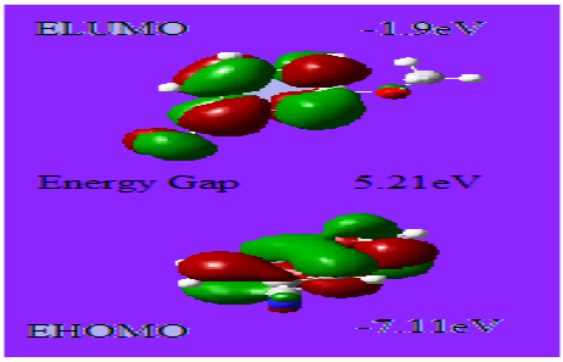

FIG.3.HOMO LUMO PLOT OF 3-METHOXYBENZONITRILE

HOMO stands for highest occupied molecular orbital which means the ability to give an electron and LUMO stands for lowest unoccupied molecular orbital which means the capability to take an electron.HOMO and LUMO are the main orbitals taking place in the chemical stability of the molecule [12]. The estimated energy gap using B3LYP 6-311++G(d,p) is 5.21eV.The energy gap explains that the title compound is experiencing charge transfer interactions and it reflects its NLO property [13]. The HOMO LUMO plot is illustrated in fig.3

E. Thermodynamic parameters

Thermodynamic parameters like entropy, enthalpy, distinct heat capacity at a consistent volume, rotational constants and thermal energy are calculated using B3LYP 6-311++G (d,p), cc-pvdz and Aug-cc-pvdz basis set and are listed in Table.5. Scaling factors are recommended [14] for calculating the zero-point vibrational energy and entropy accurately. The changes in entropy and total energy at room temperature are given in Table.5. These changes seem to be insignificant.

F. Electrostatic potential

Electrostatic potential is a useful tool to find the electrophilic (negative regions) and nucleophilic sites (positive regions) [15, 16].A plot of electrostatic potential is shown in Fig.4. An electrostatic potential plot is a tool that predicts and analyses the intra and intermolecular Fig.4.The electrostatic potential plot of 3-methoxybenzonitrile
Interactions [17]. It visualizes the relative polarity of the molecule. The various potential values are represented in various colors.The most negative potential region is represented by red colour; the

most positive potential region is represented by blue colour and the zero potential region is represented by green colour. The order of increase in potential is red - orange - yellow - green - blue [18].

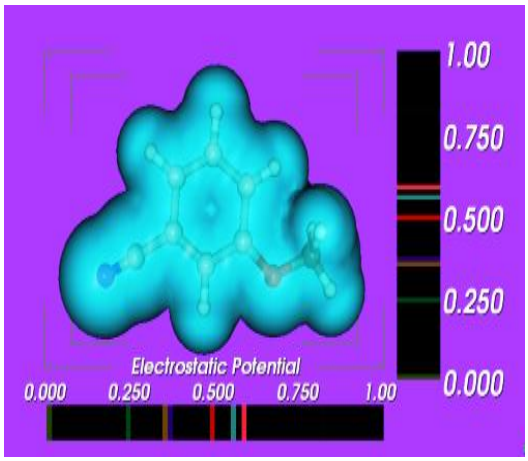

FIG.4.ELECTROSTATIC POTENTIAL PLOT OF 3-METHOXYBENZONITRILE

Figure 4 shows the electrostatic potential plot of 3-methoxybenzonitrileInteractions [17]. It visualizes the relative polarity of the molecule. The various potential values are represented in various colors. The most negative potential region is represented by red colour; the most positive potential region is represented by blue colour and the zero potential region is represented by green colour. The order of increase in potential is red - orange - yellow - green - blue [18-23].

Table.1. Geometrical Parameters Of 3-Methoxybenzonitrile

Parameters	B3LYP			Parameters	B3LYP			Parameters	B3LYP		
BondLength(Å)	6-311++G(d,p)	cc-pvdz	Aug-cc-pvdz	Bond Angle(°)	6-311++G(d,p)	cc-pvdz	Aug-cc-pvdz	Dihedral Angle(°)	6-311++G(d,p)	cc-pvdz	Aug-cc-pvdz
C1-O2	1.43	1.43	1.43	O2-C1-H11	109.5	109.5	109.5	H11-C1-O2-C3	-59.2	-60.0	-60.0
C1-H11	1.07	1.07	1.07	O2-C1-H12	109.5	109.5	109.5	H12-C1-O2-C3	60.8	60.0	60.0
C1-H12	1.07	1.07	1.07	O2-C1-H13	109.6	109.5	109.5	H13-C1-O2-C3	-179.2	180.0	-180.0
C1-H13	1.07	1.07	1.07	H11-C1-H12	109.5	109.5	109.5	C1-O2-C3-C4	30.4	-30.0	30.0
O2-C3	1.43	1.43	1.43	H11-C1-H13	109.4	109.5	109.5	C1-O2-C3-C8	-149.6	150.0	-150.0
C3-C4	1.54	1.40	1.40	H12-C1-H13	109.5	109.5	109.5	O2-C3-C4-C5	179.9	180.0	-180.0
C3-C8	1.36	1.40	1.40	C1-O2-C3	109.4	109.5	109.5	O2-C3-C4-H14	-0.1	0.0	0.0
C4-C5	1.35	1.40	1.40	O2-C3-C4	119.9	120.0	120.0	C8-C3-C4-C5	-0.1	0.0	0.0
C4-H14	1.07	1.07	1.07	O2-C3-C8	120.0	120.0	120.0	C8-C3-C4-H14	179.9	-180.0	180.0
C5-C6	1.54	1.40	1.40	C4-C3-C8	120.0	120.0	120.0	O2-C3-C8-C7	-179.9	180.0	180.0
C5-H15	1.07	1.07	1.07	C3-C4-C5	120.0	120.0	120.0	O2-C3-C8-H17	0.1	0.0	0.0
C6-C7	1.36	1.40	1.40	C3-C4-H14	120.0	120.0	120.0	C4-C3-C8-C7	0.1	0.0	0.0
C6-H16	1.07	1.07	1.07	C5-C4-H14	120.0	120.0	120.0	C4-C3-C8-H17	-179.9	180.0	-180.0
C7-C8	1.54	1.40	1.40	C4-C5-C6	120.0	120.0	120.0	C3-C4-C5-C6	0.0	0.0	0.0
C7-C9	1.54	1.40	1.40	C4-C5-H15	120.0	120.0	120.0	C3-C4-C5-H15	-180.0	180.0	-180.0
C8-H17	1.07	1.07	1.07	C6-C5-H15	120.0	120.0	120.0	H14-C4-C5-C6	-180.0	180.0	-180.0
C9-N10	1.15	1.15	1.15	C5-C6-C7	120.0	120.0	120.0	H14-C4-C5-H15	0.0	0.0	0.0
				C5-C6-H16	120.0	120.0	120.0	C4-C5-C6-C7	0.1	0.0	0.0
				C7-C6-H16	120.0	120.0	120.0	C4-C5-C6-H16	-180.0	180.0	-180.0
				C6-C7-C8	120.0	120.0	120.0	H15-C5-C6-C7	-179.9	180.0	180.0
				C6-C7-C9	119.9	120.0	120.0	H15-C5-C6-H16	0.0	0.0	0.0
				C8-C7-C9	120.1	120.0	120.0	C5-C6-C7-C8	-0.1	0.0	0.0
				C3-C8-C7	119.9	120.0	120.0	C5-C6-C7-C9	179.9	180.0	-180.0
				C3-C8-H17	120.0	120.0	120.0	H16-C6-C7-C8	179.9	180.0	180.0
				C7-C8-H17	120.0	120.0	120.0	H16-C6-C7-C9	-0.1	0.0	0.0
								C6-C7-C8-C3	0.0	0.0	0.0
								C6-C7-C8-H17	-180.0	180.0	180.0
								C9-C7-C8-C3	-180.0	180.0	180.0
								C9-C7-C8-H17	0.0	0.0	0.0

G. Non linear optical activity

For investigating the NLO activity of the material the first hyperpolarizability of the title compound was determined and compared with urea, a standard nonlinear material [25,26]. It

was found that the first hyperpolarizability of the title compound is 7.65times than urea. Based on calculations we propose that the title compound is an efficient material for NLO applications.

Table.2. NLOAnalysis Of 3-Methoxybenzonitrile

Donor (i)	Type	Ed/e	Acceptor (j)	Type	Ed/e	E(2)	E(i)- E(j)	f(i,j)
C1 - O2	σ	1.99017	C3 - C4	σ*	0.00568	2.62	1.35	0.053
C 1 - H 11	σ	1.99348	C 4 - H 14	σ*	0.01583	0.7	1	0.024
C 1 - H 13	σ	1.99111	O 2 - C 3	σ*	0.03184	2.81	0.81	0.043
O 2 - C 3	σ	1.98882	C 4 - C 5	σ*	0.01527	1.42	1.38	0.04
C 3 - C 4	σ	1.97958	C 3 - C 8	σ*	0.0212	3.46	1.27	0.059
C 3 - C 4	σ	1.97958	C 4 - C 5	σ*	0.01527	2.83	1.28	0.054
C 3 - C 4	π	1.63721	C 5 - C 6	π*	0.31623	20	0.29	0.069
C 3 - C 4	π	1.63721	C 7 - C 8	π*	0.39545	19.83	0.29	0.068
C 3 - C 8	σ	1.97726	C 3 - C 4	σ*	0.00568	3.49	1.26	0.059
C 3 - C 8	σ	1.97726	C 7 - C 8	σ*	0.0234	2.74	1.27	0.053
C 4 - C 5	σ	1.97565	O 2 - C 3	σ*	0.03184	4.03	0.99	0.056
C 4 - C 5	σ	1.97565	C 3 - C 4	σ*	0.00568	2.92	1.25	0.054
C 4 - H 14	σ	1.97579	C 3 - C 8	σ*	0.0212	3.94	1.09	0.059
C 4 - H 14	σ	1.97579	C 5 - C 6	σ*	0.01392	3.36	1.1	0.054
C 5 - C 6	σ	1.9789	C 6 - C 7	σ*	0.02533	2.74	1.25	0.052
C 5 - C 6	σ	1.9789	C 7 - C 9	σ*	0.03081	3.11	1.25	0.056
C 5 - C 6	π	1.65954	C 3 - C 4	π*	0.37118	19.47	0.27	0.066
C 5 - C 6	π	1.65954	C 7 - C 8	π*	0.39545	20.85	0.28	0.069
C 5 - H 15	σ	1.98046	C 3 - C 4	σ*	0.00568	3.63	1.08	0.056
C 6 - C 7	σ	1.96665	C 7 - C 8	σ*	0.0234	4.31	1.26	0.066
C 6 - C 7	σ	1.96665	C 9 - N 10	σ*	0.01182	4.69	1.65	0.079
C 6 - H 16	σ	1.98014	C 7 - C 8	σ*	0.0234	4.12	1.08	0.06
C 7 - C 8	σ	1.96306	O 2 - C 3	σ*	0.03184	4.19	0.99	0.057
C 7 - C 8	σ	1.96306	C 6 - C 7	σ*	0.02533	4.35	1.26	0.066
C 7 - C 8	σ	1.96306	C 9 - N 10	σ*	0.01182	4.47	1.65	0.077
C 7 - C 8	π	1.66264	C 3 - C 4	π*	0.37118	20.03	0.28	0.067
C 7 - C 8	π	1.66264	C 5 - C 6	π*	0.31623	19.3	0.28	0.066
C 7 - C 9	σ	1.97747	C 9 - N 10	σ*	0.01182	9.85	1.69	0.115
C 8 - H 17	σ	1.97695	C 3 - C 4	σ*	0.00568	4.27	1.08	0.061
C 9 - N 10	σ	1.9934	C 7 - C 9	σ*	0.03081	8.53	1.6	0.105
LP								
O2	σ	1.96902	C 3 - C 4	σ*	0.00568	4.78	1.13	0.066
O2	π	1.87705	C 1 - H 12	σ*	0.01595	5.57	0.73	0.058
O2	π	1.87705	C 3 - C 4	π*	0.37118	18.08	0.33	0.074
N10	σ	1.97216	C 7 - C 9	σ*	0.03081	11.37	1.05	0.098

Table.3.Mullikenpopulationanalysis of 3methoxybenzonitrile

S. No	Atoms	B3LYP		
		6-311++G(d,p)	cc-pvdz	Aug-cc-pvdz
1	C1	-0.329944	0.155742	1.29429
2	O2	-0.137311	-0.30946	-0.712432
3	C3	-0.1117	0.099296	-0.421852
4	C4	0.157663	0.02643	1.296497
5	C5	0.138232	0.057856	0.583528
6	C6	-0.890891	0.063773	0.773016
7	C7	2.279995	0.048631	2.156426
8	C8	-1.011654	0.081734	1.035747
9	C8	-1.114992	-0.10988	-1.00466
10	N10	-0.16781	-0.07922	-0.148654
11	H11	0.133603	0.019765	-0.189715
12	H12	0.161454	0.027899	-0.281499
13	H13	0.164076	0.026358	-0.539852
14	H14	0.154381	-0.02823	-1.08019
15	H15	0.198346	-0.02462	-0.857276
16	H16	0.167035	-0.03209	-0.966642
17	H17	0.209518	-0.02399	-0.936732

Table.4.Electric Dipole Moment, Polari ability and Hyperpolarizability Of 3-Methoxybenzonitrile.

PARAMETERS	B3LYP		
	6-311++G(d,p)	cc-pvdz	Aug-cc-pvdz
Mx	-0.1482031	-0.198701	-0.19072
By	0.7707004	0.712296	-0.77168
Mz	-2.1309955	-1.978948	-2.0986
μ=	2.2710192Debye	2.1126Debye	2.2440Debye
Axx	108.3393348	99.830006	112.3382
Axy	1.12697	3.1352383	-1.21462
Ayy	73.3755486	58.551384	77.36691
Axz	22.1685156	22.350878	22.28459
Ayz	-28.9057893	-31.14944	28.27033
Azz	125.086338	112.56179	129.1321
α0	223.41032x10-33esu	195.9019x10-33 esu	232.7491x10-33esu
α=	91.3994x10-33esu	97.8074x10-33 esu	91.4839x10-33esu
Bxxx	194.2106844	135.64128	183.9903
Bxxy	-1.3598385	15.61701	-1.02611
Bxyy	25.7466655	6.1518865	24.87196
Byyy	41.7225264	6.7573715	-34.1058
Bxxz	56.8814887	32.621075	51.99805
Bxyz	13.2962025	-0.338532	-7.5813
Byyz	-18.7205112	-37.52902	-18.8614
Bxzz	41.0818997	5.3023027	40.76783
Byzz	-55.6394187	-17.78807	42.97697
Bzzz	6.2194881	-56.48172	-2.03704
β0	2291.3614x10-33esu	1377.6041x10-33esu	2174.3574x10-33esu

Table .5. Thermodynamic parameters of 3-methoxybenzonitrile

Thermodynamic functions	B3LYP		
	6-311++g(d,p)	cc-pvdz	Aug-cc-pvdz
Self consistent field energy (a.u)	-439.085021	-439.02376	-439.051261
Zero point vibrational energy (kcal/mol)	82.24809	82.32512	82.15428
Rotational constant (ghz)	3.11645	3.09333	3.09874
	0.82542	0.82134	0.82112
	0.65531	0.65175	0.65185
Rotational temperature (k)	0.14957	0.14846	0.14872
	0.03961	0.03942	0.03941
	0.03145	0.03128	0.03128
Thermal energy (kcal/mol)			
Total	87.699	87.753	87.596
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	85.922	85.976	85.819
Specific heat capacity at constant volume (cal/mol k)			
Total	32.532	32.478	32.615
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	26.57	26.516	26.654
Dipole moment (debye)	6.2734	5.8579	6.1982
Homo(ev)	-7.11	-6.66	-6.87
Lumo(ev)	-1.9	-1.45	-1.74
Energy gap(ev)	5.21	5.21	-5.13
Entropy(s)(cal/mol k)			
Total	91.487	91.27	91.305
Translational	40.569	40.569	40.569
Rotational	29.635	29.652	29.651
Vibrational	21.283	21.048	21.084
Gibbs free energy	0.097233	0.097422	0.097156
Enthalpy	0.140702	0.140788	0.140538

IV. CONCLUSION

An accurate examination of structural, electronic and some thermodynamic property of the title compound were accomplished by DFT utilizing relevant premise sets. The first hyperpolarizability and HOMO LUMO energy gap determined by utilizing the various premise set confirmed the NLO property of the compound. The first hyperpolarizability of the title compound is 7.65times than urea. NBO analysis forms the basis for knowing the inter and intramolecular interactions in the system under study. The stabilization energy was determined from the second-order perturbation theory. Mulliken population analysis suggests that charge transfer is taking place from N, O to H.

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